

Inorganic Chemistry

including bioinorganic chemistry

Inorg. Chem., 1996, 35(7), 1751-1752, DOI: [10.1021/ic950734q](https://doi.org/10.1021/ic950734q)

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Diruthenium Cofacial Diporphyrins Axially-Bound to a Gold-Supported, Self-Assembled Monolayer Electrocatalytically Reduce Dioxide

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Supplementary Material

$(\mu\text{-N}_2)\text{Ru}_2(\text{DPB})(\text{CH}_3\text{CN})_2$: In an inert atmosphere (N_2) box, a 25-mL round bottom flask charged with $\text{Ru}_2(\text{DPB})$ (25 mg, 0.019 mmol) and acetonitrile (10 mL) was stirred for 5 h. The acetonitrile was then removed in *vacuo*. The residue was redissolved in toluene (5 mL) and stirred in the dinitrogen atmosphere for 24 h. The solvent was removed in *vacuo* leaving the dinitrogen complex (22 mg, 0.015 mmol, 79% yield). UV-VIS (CH_2Cl_2) λ_{max} 394 (Soret), 530 nm. ^1H NMR (C_6D_6) porphyrin resonances: H_{meso} 9.22 (s, 4H), 9.02 (s, 2H); $-\text{CH}_3$ 3.53 (s, 12 H), 3.14 (s, 12 H); $-\text{CH}_2\text{CH}_3$ 1.78 (t, 12H), 1.69 (t, 12H); $-\text{CH}_2\text{CH}_3$ 4.28 (m, 4H), 3.94 (m, 4H) 3.54 (m, 8H); biphenylene 7.39 (d, 2H), 7.18 (d, 2H), 6.90 (t, 2H); NCCCH_3 -3.10 (s, 6H) ppm. Addition of 2 eq. of 1-*tert*-butyl-5-phenylimidazole went cleanly to the thoroughly characterized $(\mu\text{-N}_2)\text{Ru}_2\text{DPB}(\text{*Im})_2$. Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Guillard, R.; Reed, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 2794-2796.

$(\mu\text{-N}_2)\text{Ru}_2(\text{DPA})(\text{CH}_3\text{CN})_2$: A 250-mL photolysis well charged with $\text{Ru}_2(\text{DPA})(\text{CO})_2(\text{CH}_3\text{OH})_2$ (50 mg, 0.039 mmol), benzene (20 mL), and acetonitrile (200

mL) was irradiated under an argon purge for 5 h following standard literature procedures (Anipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015-3024). The reaction mixture was then transferred to an argon-sparged side-arm flask via a cannula, and the acetonitrile removed in *vacuo*. The resulting solid was purified, in an inert (N₂) atmosphere box, by column chromatography on neutral alumina. A 50/50 mixture of acetonitrile and THF used as eluant caused the product to come off as the major dark-red band. The solvent was removed in *vacuo* and the product was stirred in toluene, open to the dinitrogen atmosphere, for 24 h. The pure product was isolated with the vacuum removal of the toluene (31 mg, 0.022 mM, 55% yield). UV-VIS (CH₂Cl₂) λ_{max} 394 (Soret), 528 nm. ¹H NMR (C₆D₆) porphyrin resonances: H_{meso} 9.07 (s, 2H), 8.99 (s, 4H); -CH₃ 3.35 (s, 12 H), 2.10 (s, 12 H); -CH₂CH₃ 1.96 (t, 12H), 1.63 (t, 12H); -CH₂CH₃ 4.10 (m, 4H), 3.87 (m, 8H) 3.52 (m, 4H); anthracene 9.00 (s, 1H), 8.74 (s, 1H), 8.33 (d, 2H), 8.07 (d, 2H), 7.58 (t, 2H); NCCCH₃ -3.04 (s, 6H) ppm. Addition of 2 eq. of 1-*tert*-butyl-5-phenylimidazole went cleanly to the thoroughly characterized (μ -N₂)Ru₂DPA(*Im)₂. Collman, J. P.; Ennis, M. S., unpublished results). This complex shows analogous chemistry and characteristics to the shorter (μ -N₂)Ru₂DPB(*Im)₂.